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(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Process for the Preparation of Plastics, Including Sheetlike Structures

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ABSTRACT OF THE DISCLOSURE

A process is disclosed for the preparation of plastics from polyesters containing (meth)acryloyl groups. The polyester has a defined composition and is heat cured in the presence of atmospheric air. Optionally, the polyester may be combined with copolymerizable monomers or other plastic precursors. The polyester is useful in forming plastic structures, e.g. shaped articles or sheet-like structures.

What Is Claimed Is:

1. A process for the preparation of plastics by curing polyesters containing (meth)acryloyl groups, characterized in that the polyesters have been prepared from:

A) 0.4 to 1.0 mol of an unsaturated dicarboxylic acid component selected from maleic acid, maleic anhydride, fumaric acid, tetrahydrophthalic acid, tetrahydrophthalic anhydride, norbornenedicarboxylic acid, norbornenedicarboxylic anhydride, or mixtures thereof;

B) 0 to 0.6 mol of a second dicarboxylic acid component, consisting of at least one aromatic or saturated (cyclo)aliphatic dicarboxylic acid having a molecular weight of 100 to 202, or at least one anhydride of such a dicarboxylic acid, or mixtures thereof;

C) 0.3 to 2.0 mol of at least one ether-alcohol component, consisting of at least one monovalent, divalent, trivalent or tetravalent ether-alcohol which has at least one ethylene oxide unit $-CH_2-CH_2-O-$ as part of an ether structure and has a molecular weight of 92 to 1000,

D) 0 to 1.7 mol of a second alcohol component, consisting of at least one monohydric, dihydric, trihydric or tetrahydric alcohol which has a molecular weight of 46 to 500 and has no ethylene oxide units as part of an ether structure; and

E) 0.5 to 6.0 mol of an unsaturated monocarboxylic acid selected from acrylic acid, methacrylic acid, or mixtures thereof

wherein the sum of the moles of components A) and B) is 1.0, the sum of the hydroxyl equivalents of components C) and D)

at least corresponds to the sum of the carboxyl equivalents of components A), B) and E), the content of olefinic double bonds in the polyesters is 5 to 17% by weight and the acid number of the polyester is between 0 and 50, and further characterized in that curing of the polyester is carried out in the presence of atmospheric oxygen at a temperature above 80°C.

2. The process according to claim 1 wherein curing of the polyester is carried out in the presence of (hydro)peroxides and siccatives.

3. The process according to claim 2 wherein curing of the polyester is carried out at a temperature above 150°C.

4. The process according to claim 1 wherein said polyesters have been prepared by reacting

0.5 to 1.0 mol of a component A),
0 to 0.5 mol of a component B),
0.5 to 2.0 mol of a component C),
0 to 1.6 mol of a component D) and
1.0 to 4.0 mol of a component E)

said polyesters having 6.5 to 15.0% by weight of olefinic double bonds and an acid number of 0 to 40.

5. The process according to claim 1 wherein the polyester is combined with other plastic precursors containing (meth)acryloyl groups prior to curing.

6. The process according to claim 1 wherein the polyester is shaped prior to curing.

7. The process according to claim 6 wherein said polyester contains inert additives.

8. The process according to claim 1 wherein said polyester is combined with copolymerizable monomers prior to curing.

9. The process according to claim 1 wherein said polyester is dissolved in an inert solvent prior to curing.

10. The process according to claim 1 wherein said polyester is emulsified in water prior to curing.

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Process for the preparation of plastics, including sheet-like structures

The invention relates to a process for the preparation of plastics by heat-curing of selected polyesters containing (meth)acryloyl groups.

Polyesters carrying (meth)acryloyl groups are known. So-called polyesteracrylates of this type, which, as described in, for example, German Offenlegungsschrift 2,838,619, 2,261,612, 3,316,593, 1,917,788, 2,033,769, 2,053,683 and 2,423,354, are obtained as reaction products of (meth)acrylic acid with diols, polyols and dicarboxylic acids, generally undergo crosslinking by means of electron beams or UV radiation. Special apparatuses are necessary for this purpose. In UV curing, the only areas cured are those which lie in the irradiation area of the UV lamps.

Curing by means of free radical formers, such as peroxides, which are cleaved by heat and/or accelerators, is normally carried out only in the absence of air, since it is otherwise impossible to obtain non-tacky and/or scratch-resistant and solvent-resistant plastics, in particular surfaces.

It was therefore the object of the invention to provide a novel process for the preparation of plastics, including sheet-like structures, from polyesters containing (meth)acryloyl groups, in which curing of the unsaturated polyesters is possible in the presence of atmospheric oxygen by a thermal method, optionally with the concomitant use of siccatives and of (hydro)peroxides.

This object was achieved by providing the process according to the invention, described in detail below. In the process according to the invention, polyesters which contain special (meth)acryloyl groups and which surprisingly are heat-curable even in the presence of atmospheric oxygen are used.

The invention relates to a process for the preparation of plastics, including sheet-like structures, by curing polyesters containing (meth)acryloyl groups, or mixtures thereof with other plastics precursors containing (meth)acryloyl groups, which polyesters or mixtures have been shaped, optionally as a mixture with inert auxiliaries and additives and/or with copolymerizable monomers and/or optionally dissolved in inert solvents or optionally emulsified in water, characterised in that the polyesters which contain (meth)acryloyl groups and which are used are those which have been prepared from

A) 0.4 to 1.0 mol of an unsaturated dicarboxylic acid component, consisting of maleic acid, maleic anhydride, fumaric acid, tetrahydrophthalic acid,

tetrahydrophthalic anhydride, norbornenedicarboxylic acid and/or norbornenedicarboxylic anhydride,

B) 0 to 0.6 mol of another dicarboxylic acid component, consisting of at least one aromatic or saturated (cyclo)aliphatic dicarboxylic acid of the molecular weight range 100 to 202 and/or at least one anhydride of such a dicarboxylic acid,

C) 0.3 to 2.0 mol of at least one ether-alcohol component, consisting of at least one monovalent, divalent, trivalent or tetravalent ether-alcohol which has at least one ethylene oxide unit $-CH_2-CH_2-O-$ as part of an ether structure and is of the molecular weight range 92 to 1000,

D) 0 to 1.7 mol of another alcohol component, consisting of at least one monohydric, dihydric, trihydric or tetrahydric alcohol which has a molecular weight of 46 to 500 and has no ethylene oxide units as part of an ether structure and

E) 0.5 to 6.0 mol of an unsaturated monocarboxylic acid component, consisting of acrylic acid and/or methacrylic acid,

with the proviso that the sum of the moles of components A) and B) is 1.0, the sum of the hydroxyl equivalents of components C) and D) at least corresponds to the sum of the carboxyl equivalents of components A), B) and E), the content of olefinic double bonds (calculated as =C=C=, molecular weight = 24) in the polyesters is 5 to 17% by weight and the acid number of the polyester is 0 to 50, and

curing of the polyester is carried out in the presence of

atmospheric oxygen at temperatures above 80°C.

In the preparation of the polyesters,
0.5 to 1.0 mol of component A),
0 to 0.5 mol of component B),
0.5 to 2.0 mol of component C),
0 to 1.6 mol of component D) and
1.0 to 4.0 mol of component E)
are preferably used, the double bond content (calculated as =C=C=, molecular weight = 24) of the polyester preferably being 6.5 to 15% by weight and the acid number of the polyester preferably being 0 to 40. The above data with regard to the acid number are based on mg of KOH/g of substance.

Component A) is preferably maleic anhydride or tetrahydrophthalic anhydride. Component B) is, for example, an acid, such as phthalic acid, hexahydrophthalic acid, isophthalic acid, terephthalic acid or adipic acid, or phthalic anhydride or hexahydrophthalic anhydride.

Component C) comprises monohydric, dihydric, trihydric or tetrahydric alcohols which have ether groups, preferably have a molecular weight of 106 to 800 and contain at least one ethylene oxide unit $-CH_2-CH_2-O-$ as part of an ether structure. Ether alcohols of this type are obtained by ethoxylation of suitable initiator molecules in a manner known per se. Suitable initiator molecules

are, in particular, the monohydric or polyhydric alcohols which correspond to the ether-alcohols and are free of ether groups. The ether-alcohols used as component C) generally have a degree of ethoxylation of 1 to 10, preferably 1 to 8, the degree of ethoxylation specifying the average number of moles of ethylene oxide which have undergone an addition reaction with 1 mole of an alcohol used as the initiator molecule. Ethoxylated diols or triols having a degree of ethoxylation of 1 to 6 and a molecular weight of 106 to 398 are particularly preferably used as component C).

Component D) comprises any monohydric or polyhydric, preferably dihydric to tetrahydric, alcohols which do not have any ethylene oxide units as part of an ether structure. The molecular weight of these alcohols is preferably 46 to 500. For example, n-hexanol, isooctanol, benzyl alcohol, ethylene glycol, propylene glycol, propane-1,3-diol, the isomeric butanediols, pentanediols, hexanediols or dimethylolcyclohexanes, trimethylolpropane, propoxylated trimethylolpropane and/or pentaerythritol are suitable.

For the preparation of the polyesters containing (meth)acryloyl groups, either all constituents A to E are heated together in an inert solvent under the conditions of an azeotropic esterification reaction until no further water separates off, or an OH-containing polyester is first prepared from the components A to D and this polyester is then allowed to react with (meth)acrylic

acid under azeotropic esterification conditions in an inert solvent until no further water separates off, or a polyester containing COOH groups is first prepared from components A and B and part of components C and/or D and the remaining components are then allowed to react with the polyester under azeotropic esterification conditions in an inert solvent until no further water separates off.

In all cases, the solvent is removed by distillation after the reaction. If necessary, aftertreatment of the end product can be carried out to obtain a lower acid number, for example the reaction with carbodiimides according to German Offenlegungsschrift 3,514,402 or with epoxides according to German Offenlegungsschrift 3,316,593.

The azeotropic esterification conditions used for the preparation of the polyester (meth)acrylates are the traditional conditions, that is to say an esterification catalyst, for example sulphuric acid or p-toluenesulphonic acid, is used and the reactants are heated in the presence of one or more inhibitors, such as hydroquinone monomethyl ether, and atmospheric oxygen (to prevent premature polymerization) in an inert solvent, such as cyclohexane, isooctane or toluene, and the water of reaction formed is removed from the system. In general, the preparation of the polyesters is carried out within the temperature range from 70 to 130°C.

The polyesters containing (meth)acryloyl groups and

obtained in this manner are in general liquid products which have a viscosity of about 1 to 100 Pa.s at 23°C.

Conversion of the unsaturated polyesters, which are plastics precursors, into cured plastics is carried out in general after a shaping procedure.

The term "plastics" is intended to embrace any three-dimensional, cured shaped articles as well as cured cement or filling compounds or sheet-like structures, in particular cured surface coatings. Accordingly, the term "shaping" is intended to include, inter alia, the production of sheet-like structures, for example of surface coatings or the processing of cements or filling compounds.

Depending on the intended use and depending on the viscosity, the polyesters containing (meth)acryloyl groups can be mixed with very different types of inert auxiliaries and additives prior to shaping. These include fillers, pigments, dyes, thixotropic agents, smoothing agents, flatting agents and levelling agents, which can be used in customary amounts. Particularly for the production of surface coatings, the polyesters containing (meth)acryloyl groups can also be used as a solution in coating solvents known per se, as a mixture with copolymerizable monomers or as an emulsion in water.

Suitable solvents are, for example, butyl acetate, cyclohexane, acetone, toluene or mixtures of such

solvents.

Examples of suitable copolymerizable monomers are organic compounds which have at least one copolymerizable olefinic double bond per molecule and have a viscosity of not more than 500 mPa.s at 23°C. These include, for example, styrene, hexane-1,6-diol diacrylate, trimethylolpropane triacrylate and N-vinylpyrrolidone.

The inert solvents and also the copolymerizable monomers can each be used in amounts of up to 100% by weight, preferably up to 50% by weight, relative to the weight of the polyesters containing (meth)acryloyl groups.

It is also possible simultaneously to use both inert solvents of the type stated by way of example and copolymerizable monomers of the type stated by way of Example.

It is also possible for the polyesters containing (meth)acryloyl groups to be mixed with other plastics precursors containing (meth)acryloyl groups, in particular urethane (meth)acrylates, prior to curing. These plastics precursors, which are optionally used, generally have a viscosity of more than 10000 mPa.s at 23°C. These additives can be used in amounts of up to 200% by weight, preferably up to 100% by weight, relative to the weight of the polyesters containing (meth)acryloyl groups.

If the polyesters containing (meth)acryloyl groups are to be processed from aqueous emulsion, the preparation of corresponding aqueous emulsions can be carried out, for example, with the aid of external emulsifiers and, optionally, customary auxiliaries used in emulsion technology.

Emulsifiers which are suitable for this purpose are known and are described, for example, in Ullmanns Encyclopädie der techn. Chemie [Ullmanns Encyclopaedia of Industrial Chemistry], Vol. 10, 4th Edition, Chapter on Emulsions, page 449 et seq.

Preferred emulsifiers are copolymerizable polyester emulsifiers containing (meth)acryloyl groups, as described in German Offenlegungsschrift 3,241,264.

The aqueous emulsions contain in general from 10 to 70% by weight, preferably 30 to 70% by weight, of the polyesters which contain (meth)acryloyl groups and are an essential feature of the invention. The preparation of the emulsions can be carried out by stirring water into the mixture of the polyester (meth)acrylate according to the invention and the emulsifier, for example simply by stirring or by means of a dissolver.

To form a finely divided emulsion, that is to say for better application of the gravitational forces, the addition of water in portions at temperatures below 30°C is advantageous. With optimal shearing, oil-in-water

emulsions are formed.

In all variants of the process according to the invention, curing is effected, optionally after evaporation of volatile auxiliaries, such as inert solvents or water, by a heat treatment at above 80°C. In a preferred embodiment, curing is assisted by the addition of polymerization initiators and of siccatives of the type known per se. Where such auxiliaries are present, curing temperatures of 80 to 160°C, preferably 90 to 150°C, are generally sufficient.

Suitable polymerization initiators are, in particular, (hydro)peroxides of the type known per se, such as tert-butyl perbenzoate, benzoyl peroxide, cyclohexanone peroxide, methyl ethyl ketone peroxide, acetylacetone peroxide, tert-butyl per-2-ethylhexanoate, bis-(4-tert-butylcyclohexyl) peroxydicarbonate, tert-butyl hydroperoxide, cumene hydroperoxide, 2,5-dimethylhexane 2,5-hydroperoxide and diisopropylbenzene monohydroperoxide. These (hydro)peroxides are preferably used in amounts of 0.5 to 3% by weight relative to the weight of the polyesters containing (meth)acryloyl groups.

The siccatives used in addition to the polymerisation initiators mentioned as examples are likewise those of the type known per se, such as, for example, cobalt salts, lead salts and manganese salts of acids such as

linseed oil fatty acids, tallow oil fatty acids and soya bean oil fatty acids, of resin acids, such as abietic acid and naphthenic acid, or of acetic acid and isooctanoic acid. They are used in the form of organic solutions in amounts such that the metal content is 0.001 to 0.1% by weight, relative to the weight of the polyesters containing (meth)acryloyl groups.

If polymerization initiators and siccatives are not concomitantly used, the temperature of the curing procedure according to the invention is in general at least 150°C, preferably 150 to 190°C. However, it is of course also possible on the one hand to use polymerization initiators and siccatives of the type stated by way of example and on the other hand nevertheless to employ the last-mentioned high temperatures in order to achieve accelerated curing.

In the Examples which follow, all percentages are based on weight.

Examples

In the Preparation Examples 1 to 5 according to the invention and Comparative Examples 6 and 7, summarised in the Table below, the starting components A), B) and D) are first heated to 150 - 185°C for 6 hours under nitrogen in the absence of other additives in the first stage in each case.

The procedure for the second stage of the process according to the invention was carried out in each case in 60% strength solution in cyclohexane in the presence of 1.5% of p-toluenesulphonic acid as a catalyst and of 0.3% of p-methoxyphenol as an inhibitor, relative in each case to the sum of the components A) to E). After the addition of components C) and E) and catalysts and inhibitors in cyclohexane, the mixture is heated at 80 to 100°C while passing through air, until no further water separates off. After the mixture has cooled, the solvent is distilled off in vacuo at 50 to 90°C.

Table 1

Starting materials (Amounts in mol)	Examples according to the invention 1	2	3	4	5	Comparative Examples 6	7
A) Maleic anhydride	1.0	0.5		1.0	1.0	1.0	
Tetrahydrophthalic anhydride			1.0				0.4
B) Phthalic anhydride		0.5					0.6
Adipic acid							
C) Ethoxylated trimethylolpropane (degree of ethoxylation: 4)	1.0	1.0	1.0	1.0	0.7		1.0
Propoxylated trimethylolpropane (degree of propoxylation: 3)						1.0	
D) Propane-1,2-diol	0.5	0.5	0.5	0.5	0.7	0.5	0.5
E) Acrylic acid	1.8	1.8	1.8		1.3	1.8	1.8
Methacrylic acid				1.8			
Properties of the polyester							
Acid number (mg of KOH/g of substance)	16	33	26	36	16	27	39
Viscosity (mPa.s 23°C)	7200	6000	16400	3600	12600	8100	2700
(Meth)acryloyl double bond content (calculated as molecular weight 24)	8.2	7.8	7.5	7.8	7.4	8.3	7.7

Use Examples 1 to 5 (according to the invention) and 6 and 7 (Comparative Examples)

1.5% of tert-butyl perbenzoate and 1% of cobalt octoate (2.2% metal content) are added to the products of the above Examples 1 to 7. After the coating films have been applied to glass sheets, they are heated for 30 minutes at 130°C. The resulting, dry coating films have a thickness of about 100 µm.

The film properties obtained are shown in Table 2.

Table 2

	Use Examples 1	2	3	4	5	Comparative Examples 6	7
Pendulum hardness (sec)[a]	120	77	45	92	160	not measurable since surface is tacky	not measurable since surface is tacky
Solvent resistance[b]	good	good	good	good	good	-	-

a) The pendulum hardnesses are determined according to König (DIN 53,157)

b) For the determination of the solvent resistance, a cotton wool ball impregnated with solvent is placed on the coating film for 1 minute. The change in the film is then evaluated by scratching with a fingernail. The solvents used are toluene, methoxypropyl acetate, ethyl acetate and acetone.

Apart from Comparative Examples 6 and 7, the surfaces of the coating films can be scratched only with difficulty, if at all.

While both hard and solvent-resistant coatings are formed with the products according to the invention, of Examples 1 to 5, the products of Comparative Examples 6 and 7 do not have adequate properties.

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